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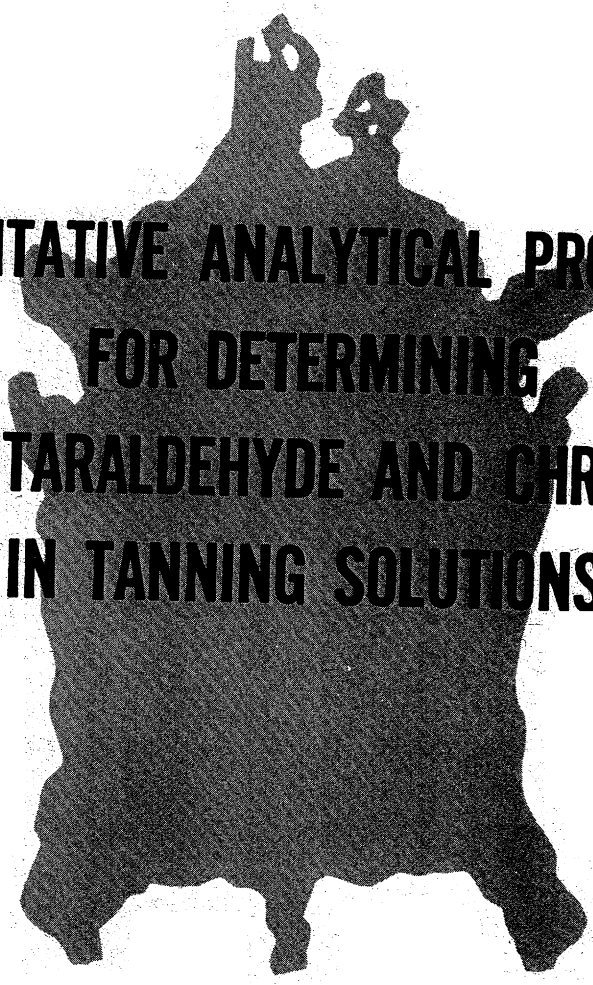

QUANTITATIVE ANALYTICAL PROCEDURE FOR DETERMINING GLUTARALDEHYDE AND CHROME IN TANNING SOLUTIONS

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ABSTRACT

Detailed directions are given for the quantitative determination of glutaraldehyde and chrome in tanning solutions. Section I outlines the precise procedure for determining glutaraldehyde. Section III describes the procedure for chrome analysis. For tanning solutions that contain both glutaraldehyde and chrome, Section II describes the use of an ion-exchange resin to remove the chrome, which interferes in glutaraldehyde determinations. Reagent and apparatus requirements are listed.

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QUANTITATIVE ANALYTICAL PROCEDURE FOR DETERMINING GLUTARALDEHYDE AND CHROME IN TANNING SOLUTIONS

by
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The method of analysis selected for determining glutaraldehyde and chrome in tanning solutions is a modification of the iodometric method described by Hunter and Potter (1). It is based on measuring the amount of aldehyde fixed by sodium bisulfite, which, when used in excess, reacts rapidly with aldehydes to form relatively stable addition products. The excess bisulfite is destroyed with iodine, and then a carefully measured excess of iodine and alkaline buffer oxidizes quantitatively both the bisulfite and the aldehyde moieties of the addition product. The remaining excess of iodine is determined by titration with standard sodium thiosulfate. A blank run (no aldehyde present) of the entire procedure is run at the same time, and difference in thiosulfate is equivalent to the aldehyde-bisulfite addition product. Basically the reactions involved are as follows:

$$RCHO \cdot NaHSO_3 + 2I_2 + 3Na_2CO_3 \longrightarrow RCOONa + Na_2SO_4 + 4NaI + 3CO_2 + H_2O$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

The presence of chrome tanning salts in the tanning solution interferes with the determination of glutaraldehyde. This is due, probably, to the susceptibility of some of the complex chrome compounds to oxidation during an iodometric analytical procedure such as used in determining glutaraldehyde. It has been found (2, 3) that the chrome could be removed from the analytical sample by using an ion-exchange resin in a small column. In some cases, where appreciable masking agents such as sodium acetate and sodium formate are present, a little chrome may get through the column and

give the sample a very slight bluish cast. The amount of chrome getting through is usually negligible. When the glutaraldehyde passes through the column the effluent is ready for iodometric analysis.

Although the chrome analysis in Section III was developed for the analysis of tanning solutions containing both chrome and glutaraldehyde, it is fully satisfactory for use when no glutaraldehyde is present. The procedure described in Section III, a modification of one found in the literature (4), is suitable for determining chrome in small samples of tanning solutions. The analysis is fairly simple and rapid and avoids the use of relatively dangerous oxidizing agents.

I. DETERMINATION OF GLUTARALDEHYDE IN CHROME-FREE TANNING SOLUTIONS

Reagents:

1. Distilled water

2. Sodium bisulfite ($NaHSO_3$) solution, approx. 0.1N, (10.4 gram/liter). This solution should be stored in a glass-stoppered bottle and should be no more than 2 weeks old when used in the analysis.

3. Starch solution. Prepare as follows: Make a slurry of 0.5 grams of soluble starch (reagent grade) in 10 ml. of water. Add this slurry to 40 ml. of boiling water. When the solution clears, cool it to room temperature and add 1 gram of potassium iodide (KI). For convenience, store this solution in a bottle fitted with a combination glass stopper-medicine dropper. Discontinue use of this indicator when it begins to get cloudy or develops color (in about 3 to 10 days).

4. Iodine solution, approx. 0.1N (12.7 gram/liter). Prepare as follows: Weigh the iodine in a 200 ml. beaker on a simple laboratory balance (such as a Harvard or Triple beam, but never on an analytical balance), then add about 22 grams of potassium iodide. Dissolve the mixture in about 50 ml. of distilled water. Stir occasionally until all the iodine is dissolved. Do not heat the solution. Dilute the solution to 1 liter in a flask or cylinder. Filter this solution and transfer to dry, glass-stoppered bottles (dark glass, if possible) and store away from light when not in use. A portion

of this iodine solution may be standardized against the standard sodium thiosulfate and then used for back titration.

5. Sodium carbonate solution (Na_2CO_3), approx. 2N, (124 grams sodium carbonate monohydrate/liter).

6. Sulfuric acid solution (H_2SO_4), approx. 1N, (27.8 ml. concentrated reagent grade sulfuric acid/liter.

7. Sodium thiosulfate solution ($Na_2S_2O_3$), O. 1N, Standardized. Standard solutions and standard concentrates are now available from many laboratory chemical supply dealers. These are very convenient and time-saving. However, for preparation of standard solutions in the laboratory, see an analytical chemistry (quantitative) text book for exact directions. This reagent must be a standardized solution, because all calculations are based on the exact amount used. (See calculations.)

Apparatus:

Pipet, Class A - 1 ml. (precision accuracy required).

Buret, precision bore - 50 ml. (precision accuracy required).

Erlenmeyer flasks, and glass stoppers - 200 ml. size (2 required for each analysis).

Pipets, standard grade - (2) 5 ml., (2) 10 ml.

Buret. standard grade - 50 ml.

Volumetric flask, Class A - 5 ml., (Precision accuracy required).

Auxiliary items such as beakers, flasks, and stirring rods, wash bottle, etc., as may be convenient or indicated in the analytical procedure.

Tanning Solutions

The iodometric method (5) was adapted to determine the amount of glutaraldehyde present in small, dilute samples. Most samples from tanning liquors that contained, at the

start of the run, 6 percent (on DW or DPW*) glutaraldehyde (25 percent commercial solution) in a 1:1 or 1:2 float, fall into the proper concentration range. For more concentrated samples, a simple modification is described in the following procedure.

The analysis does not appear to be affected much by the presence of the salts usually found in tanning solutions. Buffering and masking agents do not interfere appreciably if the sample, at the start of the analysis, is adjusted to a pH of 5.0 or below. When and how to make this adjustment is outlined in the paragraph following the calculations.

Analysis

A suitable quantity of the tanning solution is filtered into a small bottle. One-ml. samples used in the analysis are pipetted from this bottle. At times, certain samples require dilution before analysis. This is true whenever the results of an analysis indicate the tanning solution to be more concentrated than about 0.10 millimole of aldehyde/ml. for the dialdehydes or about 0.20 millimole of aldehyde/ml. for formaldehyde. The sample withdrawn early during the run, when the tanning liquor is more concentrated than 1 percent active glutaraldehyde, must be diluted. In such cases 1.0 ml. of the tanning solution is diluted to 5.0 ml. (in a volumetric flask) and then 1.0 ml. of the diluted solution is used in the analysis. Each analysis and blank is run in duplicate. Use precision pipets, burets, and volumetric flasks. The details of the procedure follow:

Precisely 1 ml. of filtered tanning solution is pipetted into a 200 ml. Erlenmeyer flask to which is added 10 ml. of distilled water, followed by 5 ml. of $NaHSO_3$. Allow a reaction time of 15 minutes and add about 5 to 7 drops of starch solution as an indicator. Wash the stopper and neck into the flask and add the iodine solution carefully from a buret to the endpoint (very pale blue) to destroy excess bisulfite. If this endpoint is overshot, readjust with the dropwise addition of sodium bisulfite solution. No record of this adjustment need be kept. When the endpoint is satisfactory, add precisely 10 ml. of the same iodine solution with a pipet and be sure to use the same pipet for the blank determination. Next, add

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* DW = drained weight; DPW = drained pickled weight.

5 ml. of Na_2CO_3 solution, stopper the flask and place in the dark (i.e., cabinet) for 20 - 30 minutes. (If the solution becomes colorless during this interval, this is an indication that too much aldehyde is present. The original solution must be diluted accurately as described above, and the analysis repeated). Add 10 ml. of H_2SO_4 to acidify the solution. Test a drop of the solution on indicator paper to make sure the reaction mixture is acidic and add additional acid dropwise, if needed. Replace the stoppered flask in the dark for an additional 10 minutes. Finally, titrate the entire contents of the flask carefully with standard sodium thiosulfate to the endpoint. Standardized iodine solution must be used to back-titrate if the endpoint is overshot with sodium thiosulfate. Accurate record of the back titration must be kept and taken into account in the final calculations.

Simultaneously a blank is run, exactly as described above without the addition of the tanning solution sample.

The data from the analysis are used in the formula shown below. Note that the value for the concentration of the sodium thiosulfate is the only one used in the calculation; hence, this must be a standardized solution.

Calculations:*

1) $\frac{N}{4A}(V-V^1) = \frac{\text{millimoles of aldehyde}}{S}$,

2) $\frac{N}{4A}(V-V^1) \times \frac{MW}{1000}$ = grams aldehyde/S,
for a 1 ml. sample of glutaraldehyde:
A = 2; MW = 100; S = 1.

3) $\frac{N}{8}(V-V^1) \times \frac{100}{1000}$ = grams glutaraldehyde/ml.,
which is equivalent to:

4) $\frac{N}{8}(V-V^1) \times \frac{100}{1000} \times 100$ = grams glutaraldehyde/100 ml.

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* These calculations do not show corrections for back-titrations.

Simplifying, this becomes:

5) $\frac{N}{8}$ $(V-V^1)$ x 10 = grams glutaraldehyde/100 ml.

If the sample of glutaraldehyde solution must be diluted, the dilution factor is applied in the formula; i.e., when the sample is diluted 1:5, the factor becomes 5 as used below:

6) $\frac{N}{8}$ $(V-V^1) \times \frac{100}{1000} \times 100 \times 5$ = grams glutaraldehyde/ 100 ml.

Simplifying, this becomes:

7) $\frac{N}{8}$ $(V-V^1) \times 50$ = grams glutaraldehyde/100 ml., (Report to 2 decimal places; i.e., 0.47 gram/100 ml.)

S = sample size.
N = normality of sodium thiosulfate solution.
V = volume of sodium thiosulfate solution to titrate the blank.
V^1 = volume of sodium thiosulfate solution to titrate the sample.
A = number of aldehyde groups in molecule - (for glutaraldehyde, A=2; glyoxal, A=2; formaldehyde, A=1).
MW = molecular weight: glutaraldehyde = 100; formaldehyde = 30; glyoxal = 58.

The procedure outlined above is followed in analyzing tanning solutions at pH 5 or below. Samples from tanning solutions with a pH above 5 must be acidified. This is done immediately after the addition of the 10 ml. of distilled water mentioned at the beginning of the analytical procedure. Sulfuric acid is added dropwise to the solution until the pH falls to 5.0 or less. The number of drops of acid required must be determined before hand on a separate, accurately measured and diluted sample with a pH meter or indicator. The acidified sample may then be analyzed as described above.

The procedure outlined may be adapted for analysis of formaldehyde and glyoxal.

II. DETERMINATION OF GLUTARALDEHYDE IN TANNING SOLUTIONS CONTAINING CHROME

Reagents:

Dowex 50 or 50 W (or equivalent), mesh size 20 - 50, Na form.

Distilled water.

Sodium chloride (NaCl), 5% solution.

Silver nitrate ($AgNO_3$), approx., 0.25N,(4.3g/100 ml.).

Apparatus:

Ion-exchange tubes (see fig. 1).

Wash bottle (for distilled water).

Rubber stoppers (for tubes).

Erlenmeyer flasks, 200 ml. size with 24/40 ground glass joints and stoppers to fit. Two flasks required for each test.

Analysis:

The ion-exchange column is made up as follows (see fig. 1):

A glass tube about 36 cm. long with an inside diameter of about 10 mm., is fitted at narrowed, lower end, with a needle-valve (Teflon*) or with tubing and screw clamp. A small plug of glass wool is inserted to the narrow junction of the tube and then a slurry of Dowex 50 in distilled water is poured in to a depth of about 20 cm. The resin must be poured in carefully and then kept under distilled water at all times to avoid entrapment of air bubbles and formation of channels. The space remaining above the resin is large enough to hold 5 ml. portions of distilled water used to elute

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* Mention of specific firms and products in this report does not imply endorsement by the United States Department of Agriculture to the possible detriment of others not mentioned.

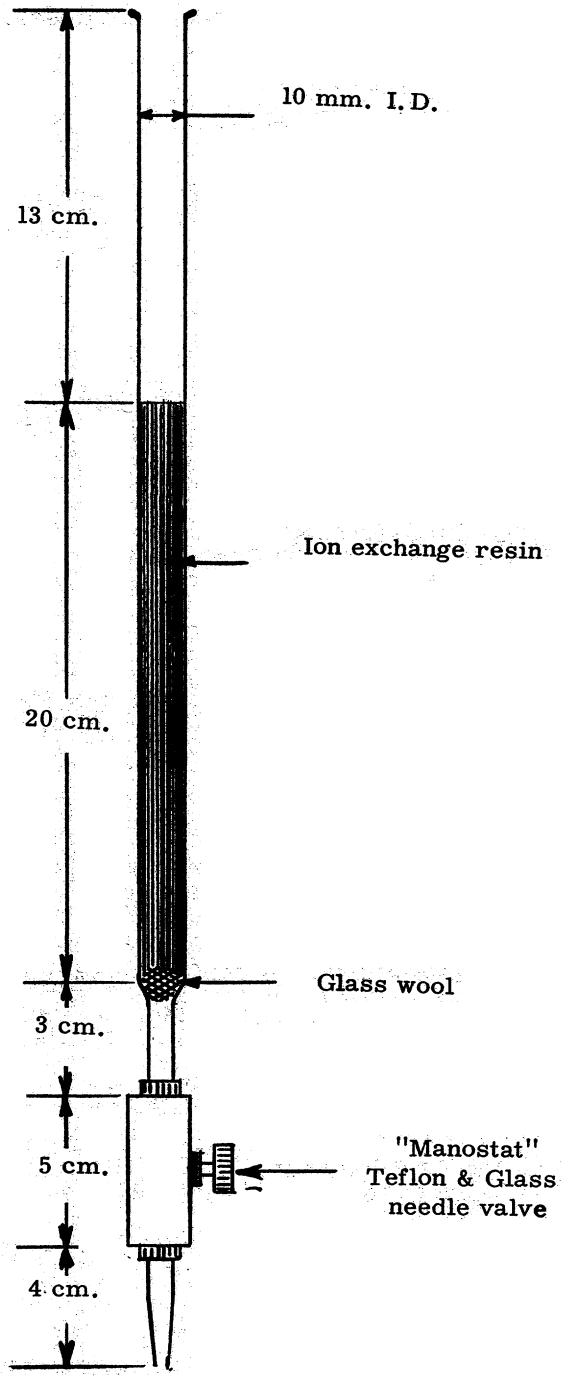

Fig. 1. Ion-Exchange Column

the sample. With tubes set up as described above, the procedure is as follows:

With the water level in the tube even with the top of the resin, add 1.0 ml. of tanning liquor sample, accurately measured with a precision pipet. Remove and collect sufficient water from the bottom of the tube, dropwise, into a 200 ml. Erlenmeyer flask, until the sample is lowered into the resin bed. The sample and resin bed should now have the same upper level. After about 5 minutes, add very slowly 5 ml. of distilled water to the tube and begin collecting, dropwise, the solution from the bottom of the column (into the same Erlenmeyer flask). Adjust the dropping rate into the flask to about 10 to 12 drops per minute. As the water level approaches the resin level, add another 5 ml. portion of distilled water. This is continued until a total of 40 ml. of water has been added and an equal amount of solution collected. Close the valve or screw clamp when the water level drops to the top of the resin bed. Add a little distilled water to the column, and close the tube with a stopper to be sure the entire resin bed is kept wet with distilled water and ready for the next sample. Each analysis is run in duplicate.

The solution collected in the flask is ready for glutaraldehyde analysis according to the procedure described in section I. However, the 10 ml. dilution step at the beginning should be omitted. The blank should contain 40 ml. of distilled water to maintain a volume equal to that of the samples to be analyzed.

The ion-exchange resin is replaced or regenerated after about 5 to 8 samples are run through. The resin removed is regenerated with sodium chloride (NaCl) solution as directed by the resin supplier (6, 7).

III. DETERMINATION OF CHROME IN TANNING SOLUTIONS

This procedure is designed for the analysis of samples containing from 0.01 to 0.045 gram Cr_2O_3. Tanning solution samples of 2 to 3 ml. (from the beginning of the tanning run) to 25 ml. (from near end of run) are used. This is based on using from 4 to 6 percent (DW or DPW) of a chrome tanning agent, which is approximately 25 percent Cr_2O_3, in a 1:1 float tanning bath.

Reagents:

1. Distilled water.

2. Sodium hydroxide (NaOH) approx. 2N, 60 grams of sodium hydroxide dissolved in 750 ml. of water.

3. Hydrogen peroxide (H_2O_2), approx. 6 percent, 80 cc. hydrogen peroxide (30%) dissolved in 320 ml. of water.

CAUTION: Note all precautions on bottle labels when handling 30% hydrogen peroxide. The 6% hydrogen peroxide is also irritating to the skin.

4. Nickelous nitrate ($Ni(NO_3)_2$), approx. 5 percent, 24 grams $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in 300 ml. of water.

5. Hydrochloric acid (HCl), concentrated.

6. Potassium iodide (KI), approx. 1N, 49.8 grams of potassium iodide dissolved in 300 ml. of water.

7. Starch solution-indicator - See (3) under "Reagents" in section I.

8. Sodium thiosulfate solution ($Na_2S_2O_3$), 0.1N, Standardized - See (7) under "Reagents" in section I.

9. Iodine solution, Standardized - see (4) under "Reagents" in Section I.

Apparatus:

Erlenmeyer flasks, 250 ml. size, with 24/40 ground glass joints and glass stoppers, 2 flasks (each sample run in duplicate).

Water cooled condensers to fit.

Pipets, Class A-3,5, 10ml. (precision accuracy required).

Pipets, standard grade - 20 ml., 50 ml. (or graduate cylinder).

Pipets, standard grade - 2 ml., 5 ml.,

Hot plate.

Buret, precision bore - 50 ml. (precision accuracy required).

Analysis:

Filter the tanning solution and transfer the proper size sample, accurately measured with a precision pipet, to a 250 ml. Erlenmeyer flask. Make the solution alkaline with 20 ml. of NaOH and add 50 ml. of freshly prepared H_2O_2. Reflux the solution for about 10 minutes. During this interval, a pure-yellow chromate color appears. Add a few drops of nickel nitrate solution through the top of the condenser. If there is excessive foaming, wait until it subsides before adding a few more drops.

When the foaming definitely becomes moderate, add slowly about 5 ml. of the nickel nitrate. (The nickel nitrate helps destroy the excess peroxide.). When most of the evolution has stopped, boil the contents of the flask for 3 minutes, then allow it to cool. Run a little distilled water from a wash bottle down the condenser into the flask. Remove the flask and cool it to room temperature. This can be hastened by immersing the flask in running water. Add 10 ml. HCl and cool the flask again then add 2 ml. of KI solution. Place the stoppered flask in the dark for 15 minutes, then titrate the entire contents of the flask with standard sodium thiosulfate. Use about seven drops of starch solution as indicator.

The sodium thiosulfate titration must be done carefully, to a pale blue endpoint, with a precision buret. If the solution becomes a definite pale green, the endpoint was passed and back titration with standard I_2 is necessary. The final calculations are based on the exact amount of sodium thiosulfate used and its normality, with a correction for back titration, if any. The calculations are based on the following formulae:

$$K_2Cr_2O_7 + 6KI + 14HCl \longrightarrow 8KCl + 2CrCl_3 + 7H_2O + 3I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

$$I \rightleftharpoons \frac{Cr_2O_3}{6}$$

$$\frac{V \times N \times 0.02533}{\text{ml. sample}} = Cr_2O_3 \text{ gram/ml.}*$$

V = ml. sodium thiosulfate.

N = normality of sodium thiosulfate.

0.02533 = factor for Cr_2O_3.

Multiply result by 100 to get Cr_2O_3 in grams/100 ml.

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* This formula does not show correction for back titration.

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